# FLAME RETARDANT COMPOSITIONS

DESCRIPTION

Phenyl silsesquioxane resins are well known in the art as attractive non-halogen fire

5   retardants for aromatic containing thermoplastics such as polycarbonate. However, they

currently must be used with a Teflon® additive to prevent dripping during initial burn in

order to successfully meet desired UL 94 VO status. The Teflon® additive, a halogen-

containing material, not only adds cost but also reduces transparency of clear thermoplastics

such as polycarbonate. It has been discovered that silicon-bonded hydrogen-containing

10   phenyl silsesquioxane resins provide UL94 VO status to polycarbonate without the use of

Teflon® enabling a transparent non-halogen solution to this need. In addition, these materials

harden the char and thus lower the rate of heat release, of char forming polymers such as

polyesters including polycarbonate, polybutylene terephthalate (PBT), polycyclomethylene

terephathalate (PCT), polyethylene terephthalate (PET), polymers such as polyether sulphone

15   (PES), polyphenylene sulfide (PPS), polyphenylene ether (PPE), and phenolics, nitrogen

containing polymers such as thermoplastic urethanes (TPUs) and polythalamides among

others.

The patents and publications that form the background art for this invention are

EP 1 026 204 A2, Japanese Patent Publication No. 2000212460 A, Japanese Patent

20   Publication No. 11140294 A, Japanese Patent Publication No. 2000226527 A, Japanese

Patent Publication No. 2001031771 A2, EP 0 918 073 A2, Japanese Patent Publication No.

10139996 A, EP 0 829 521 A1, Japanese Patent Publication No. 2000302961 A, PCT Patent

Publication No. WO99/28387, Japanese Patent Publication No. 11217494 A2, Japanese

Patent Publication No. 2001152004 A2, Japanese Patent No. 3048738 B2, PCT Patent

25   Publication No. WO99/40158, U.S. Patent No. 5,100,958, EP 1 094 093 A2,

EP 1 127 921 A1, NEC Publication Polymers Advanced Technology Vol. 9, pages 593-600

(1998), and NEC Publication NEC Research. & Development Vol. 39, No. 2, April 1998.

This invention relates to a flame retardant composition comprising: (a) 81 to 99.99

weight percent of a thermoplastic resin, thermoset resin, thermoplastic resin blend, or

30   thermoset resin blend which upon burning forms a char and (b) 0.01 to 19 weight percent of a

silsesquioxane resin having a weight average molecular weight of greater than 300 and

having the average molecular formula:

$$(R_3SiO_{1/2})_a \ (R_2SiO_{2/2})_b \ (RSiO_{3/2})_c \ (SiO_{4/2})_d \ (RO_{1/2})_e \ (OH_{1/2})_f$$
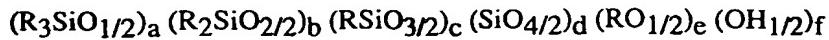
wherein each R is hydrogen, an alkyl group, an alkenyl group, or an aryl group having from 6 to 12 carbon atoms, a and b are zero or positive numbers and the value of a+b is greater than zero, c is a positive number, and d, e and f are zero or positive numbers with the provisos that the copolymer comprises at least 40 mole percent of $RSiO_{3/2}$ units, the copolymer comprises less than 10 mole percent $SiO_{4/2}$ units, greater than 30 mole percent of the silicon-bonded R groups are silicon-bonded aryl groups, greater than 0.5 mole percent of the silicon-bonded R groups are silicon-bonded hydrogen atoms, the content of silicon-bonded hydroxyl groups is equal to or less than 2 weight percent, and the content of silicon-bonded alkoxy groups where the alkoxy group is methoxy or ethoxy is equal to or less than 5 weight percent.

Component (a) is a thermoplastic resin, thermoset resin, thermoplastic resin blend, or thermoset resin blend which upon burning forms a residue (char). This char is improved by using Component (b), to be harder and thus lower the rate of heat release due to less fuel evolving per unit time during burning. Ideally, the char would ceramify to a glass and "insulate" the surface from the external flux and other ignition sources and thus have a lower Heat Release Rate.

Component (a) can be a thermoplastic resin exemplified by polycarbonates, polyamides exemplified by Nylons such as polycaprolactam (Nylon-6), polylauryllactam (Nylon-12), polyhexamethyleneadipamide (Nylon-6,6), and polyhexamethylenedodecanamide (Nylon-6,12), and blends of Nylons with other polymers, polyesters exemplified by polybutylene terephthalate (PBT), polyethylene terephthalate (PET), and polyethylene naphthalate (PEN), blends of polycarbonates with other polymers as exemplified by polycarbonate-acrylonitrile-butadiene-styrene (PC/ABS) blends and polycarbonate-polybutylene terephthalate (PC/PBT) blends, polyphenylene ether (PPE), polyphenyleneoxide (PPO), and blends of PPE or PPO with styrenics such as HIPS, polystyrene, acrylonitrile-butadiene-styrene (ABS), SAN, polyphenylene sulfide (PPS), polyether sulphone (PES), polyaramids, polyimides, phenyl-containing resins having a rigid rod structure, styrenic materials exemplified by ABS (acrylonitrile-butadiene-styrene), polystyrene (PS), and high-impact polystyrene (HIPS), polyacrylates, styrene-acrylonitrile resins (SAN), halogenated plastics exemplified by polyvinyl chloride, fluoroplastics, and any other halogenated plastics, polyketones, polymethylmethacrylate (PMMA), thermoplastic

elastomers such as thermoplastic urethanes, thermoplastic vulcanizates, and styrene ethylene butylene styrene (SEBS) copolymer, and natural products such as cellulosics, rayon, and polylactic acid. Component (a) can also be a blend of any of the thermoplastic resins described above.

5   Component (a) can also be a thermoset material. The thermoset material exemplified by epoxy resins, phenolic resins, urethane elastomers, and blends thereof, and also includes any thermoset material which involves mixing one component with another allowing curing to make a thermoset material and component (b) is therein.

In the formula for Component (b), R can be a hydrogen atom, an alkyl group

10   exemplified by methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, and dodecyl, an alkenyl group exemplified by vinyl, allyl, butenyl, pentenyl, hexenyl, octenyl, and decenyl, or an aryl group having from 6 to 12 carbon atoms exemplified by phenyl, naphthyl, methylphenyl, ethylphenyl, chlorophenyl, bromophenyl and fluorophenyl.

Component (b) can thus be selected from

15     $(Me_2HSiO_{1/2})_a(PhMeSiO_{2/2})_b(Me_2SiO_{2/2})_b(PhSiO_{3/2})_c$,

$(MeHSiO_{2/2})_b(PhSiO_{3/2})_c$, or

$(Me_3SiO_{1/2})_a(MeHSiO_{2/2})_b(PhSiO_{3/2})_c$.

The copolymer comprises at least 40 mole percent of $RSiO_{3/2}$ units, with copolymer typically comprising from 60 mole percent to 90 mole percent of $RSiO_{3/2}$ units. The

20   copolymer comprises less than 10 mole percent $SiO_{4/2}$ units, and typically the copolymer will comprise less than 5 mole percent of $SiO_{4/2}$ units. Greater than 30 mole percent of the silicon-bonded R groups are silicon-bonded aryl groups and typically from 50 to 80 mole percent of the silicon-bonded R groups are silicon-bonded aryl groups. Greater than 0.5 mole percent of the silicon-bonded R groups are silicon-bonded hydrogen atoms, with the mole

25   percent of silicon-bonded R groups that are silicon-bonded hydrogen atoms typically being from 1 to 5 mole percent. The content of silicon-bonded hydroxyl groups is equal to or less than 2 weight percent, and is typically from 0.5 to 1.2 weight percent. The content of silicon-bonded alkoxy groups where the alkoxy group is methoxy or ethoxy is equal to or less than 5 weight percent.

30   The siloxane resin of Component (b) is prepared by methods well known in the art such as those described, for example, in the *Silicone Handbook*, Chapters 12 and 13 (pp 466-

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515) edited by Kunio Ito (Nikkan Kogyo Shinbun-sha (1990)). These methods include the hydrolysis of mixtures containing the corresponding chlorosilanes or alkoxysilanes and continuing the reaction until the desired molecular weight is achieved.

The flame retardant compositions of this invention can further comprise a sodium-

5   containing catalyst. The sodium-containing catalyst is exemplified by organosodium materials such as sodium toluene sulfonate, or sodium stearate. The amount of catalyst used can be from 0.005 to 2 weight percent, but generally comprise from 0.01 to 0.05 weight percent, said weight percent being based on the total weight of the composition.

The flame retardant compositions of this invention can further comprise

10   polytetrafluoroethylene powder (TEFLON®) or Dyneon®TF PTFE). The flame retardant compositions of this invention may comprise up to 10 weight percent of polytetrafluoroethylene powder, but generally comprise from 1 to 3 weight percent of polytetrafluoroethylene powder, said weight percent being based on the total weight of the composition. The flame retardant compositions of this invention are useful as clear housings

15   for electronic devices such as computer monitors or housings, should the compositions be clear. Otherwise the compositions are useful as fire resistant compositions in a variety of electronic devices. Relatively low loadings of polytetrafluoroethylene powder were used in the examples disclosed here to maintain moderate to high clarity.

The Fire Test in the Examples hereinbelow was the test described by Underwriters

20   Laboratories Corporate Headquarters 333 Pfingsten Road Northbrook, IL 60062-2096 USA (UL94). A description of the test is included by reference to UL.

An additional fire test, ASTM E 1354, described by American Society for testing and Materials 1916 Race St, Philadelphia, PA 19103. A description of the test is included by reference to the ASTM.

25   Ingredients:

Thermoplastic Resins:

CALIBRE® 200-22 (polycarbonate resin)

MAGNUM® 941 (acrylonitrile-butadiene-styrene resin), and

PELLETHANE® 2355-75A (polyurethane elastomer resin)

30   all which are available from The Dow Chemical Company, Midland, Michigan.

TEFLON® 6C (polytetrafluoroethylene powder made by E. I. DuPont de Nemours of Wilmington, Del.)

EMERGE® 8500 (translucent, ignition resistant polycarbonate available from The Dow
Chemical Company, Midland, Mi.).

AMOCO® 4018 (Polypropylene homopolymer, having a density of 0.906 g/cc and a melt
flow index of 13.5, Amoco Oil Company Corporation, Chicago, Ill.)

5   CRASTIN® 6129 (thermoplastic polyester resin made by E. I. du Pont de Nemours and
Company Wilmington Delaware).

ELTESOL ST-90 (sodium toluene sulfonate available from Albright & Wilson Company).
This was used as the Char Catalyst in the Examples below.

The masterbatches containing the siloxane resin were prepared using each of the

10   resins below with the following formulation:

Masterbatch	Formulation
Thermoplastic Resin or	
Thermoplastic Resin Blend	balance to 100 weight percent
Silsesquioxane Resin	8, 10 or 50 weight percent
Char Catalyst	Zero or 0.3 weight percent
Polytetrafluoroethylene Powder	Zero or 3.0 weight percent

Procedure for preparing Masterbatch:

Heat Haake bowl to 220 °C or about 50°C above Tg (glass transition temperature) of the

20   candidate plastic or blend.

Place Thermoplastic Resin or Thermoplastic Resin Blend into the bowl and bring it to a melt
using 100 rpm mixing.

Place Silsesquioxane Resin in bowl, mix for about 2 minutes.

Add Char Catalyst.

25   Add Polytetrafluoroethylene Powder (if desired) and mix 5 minutes.

Remove Masterbatch cool and powder/pelletize in chopper.

The Masterbatch was then mixed with the appropriate thermoplastic resin at a weight ratio of
thermoplastic resin to Masterbatch of 10:1 in a twin-screw extruder.

UL 94 Fire Test Specimens

Injection molded 3.2 mm bars and a 4X4 inch 1 mm thick plaque. The plaques were cut to 0.5-inch wide rectangular specimens and the edges sanded to minimize fibrils.

5 **Fire Testing**

UL 94 Fire Test described above.

ASTM E 1354 Fire Test Specimens

Injection molded 4X4 inch X 3/16-inch thick (100x100x9.75 mm) plaque.

Fire Testing

10 ASTM E 1354 Fire Test described above administered at 90 kW/m2 cone external heat flux on a Dark Star model Cone Calorimeter software modified by Fire Testing Technology Limited P.O. Box 116, East Grinstead, West Sussex, RH19 4FP, United Kingdom.

Example 1

15 Masterbatch containing a silsesquioxane resin having the average molecular formula

$(Me_2HSiO_{1/2})_{0.20} (PhSiO_{3/2})_{0.78} (PhMeSiO_{2/2})_{0.01} (Me_2SiO_{2/2})_{0.01}$

where Me denotes methyl and Ph denotes phenyl.

Isopropanol (559.5 g) was added to phenyltrichlorosilane (1970.8 g), then diluted with toluene (1924.7 g). This mixture was added to heated (to a temperature of 50 °C) deionized

20 water (6737.4 g) and the resulting reaction mixture heated to 65 °C for one hour. The aqueous phase was removed and the organic phase washed with deionized water and saturated aqueous $NaHCO_3$. To facilitate the final separation, additional toluene (1082 g) was added. Residual water was removed from the organic phase via azeotropic distillation and the reaction product concentrated to a ~ 65 wt% solution. Dimethylchlorosilane

25 (450.1 g) was added to a portion of this solution (1500.1 g) and the mixture heated to 35 °C for 4.5 hours, then stirred at ambient temperature for three days. Volatiles (250 g) were removed by distillation, then isopropanol (150 g) and toluene (480 g) added. Additional volatiles (668 g) were removed by distillation. Deionized water (97.5 g), dimethoxyethane (500 g) and toluene (160 g) were added, then all volatile materials removed by distillation at

30 ambient pressure, then under reduced pressure. The hot molten product was poured onto a

cooled metal surface. The resulting product was isolated as a friable solid. The product was identified by ^{29}Si NMR as a silsesquioxane resin having the average molecular formula: $(Me_2HSiO_{1/2})_{0.20} (PhSiO_{3/2})_{0.78} (PhMeSiO_{2/2})_{0.01} (Me_2SiO_{2/2})_{0.01}$ where Me denotes methyl and Ph denotes phenyl. This silsesquioxane resin was then used to prepare a

5   Masterbatch according to the procedure outlined above. The Masterbatch, produced with 8 weight percent of the candidate resin and 0.3 weight percent char catalyst, was then mixed with a thermoplastic resin at a weight ratio of thermoplastic resin to Masterbatch of 10:1 in a twin-screw extruder, molded according to the UL 94 test piece procedure and subjected to UL94 Flame Test. The final formulation is shown in Table 1 below. The results are shown in

10   Table 2 below.

Example 2

Masterbatch containing a silsesquioxane resin having the average molecular formula $(MeHSiO_{2/2})_{0.25}(PhSiO_{3/2})_{0.75}$ where Me denotes methyl and Ph denotes phenyl.

15   Phenyltrimethoxysilane (813.5 g) was hydrolyzed with deionized water (346.7 g) in the presence of trifluoromethanesulfonic acid (2.03 g). Volatile material (1006.2 g) was removed via distillation. After cooling to 50 °C, toluene (892.4 g) and additional deionized water (173.3 g) were added. Additional volatile material was removed via distillation to a reaction mixture temperature of 75 °C. Additional toluene (671.9 g), methylhydrogen cyclic

20   siloxanes $(-(MeHSiO)_x-)$ (404.5 g), and glacial acetic acid (404.5 g) were sequentially added and the reaction mixture stirred at 75 °C for five hours, then washed with deionized water, aqueous NaHCO$_3$ and more deionized water. Residual water in the organic phase azeotropically removed, then the organic solvent removed by stripping under reduced pressure to yield 2915.5 grams of a solid material. The solid material was identified by ^{29}Si

25   NMR as a silsesquioxane resin having the average molecular formula: $(MeHSiO_{2/2})_{0.25}(PhSiO_{3/2})_{0.75}$ where Me denotes methyl and Ph denotes phenyl. This silsesquioxane resin was then used to prepare a Masterbatch, produced with 8 weight percent of the candidate resin and 0.3 weight percent char catalyst, according to the procedure outlined above. The Masterbatch was then mixed with the thermoplastic resin at a weight

30   ratio of thermoplastic resin to Masterbatch of 10:1 in a twin-screw extruder, molded

according to the UL 94 test piece procedure and subjected to UL94 Flame Test. The final
formulation is shown in Table 1 below. The results are shown in Table 2 below.

Example 3

5   Masterbatch containing a silsesquioxane resin having the average molecular formula
$(Me_3SiO_{1/2})_{0.10}(MeHSiO_{2/2})_{0.19}(PhSiO_{3/2})_{0.71}$ where Me denotes methyl and Ph denotes
phenyl.

Phenyltrimethoxysilane (396 g) was reacted with water (54 g) in the presence of
toluene (300 g) and trifluoromethanesulfonic acid (0.2 g) and heated to 70 °C. Volatiles were
10   removed via distillation at this temperature over a three-hour period. Additional toluene (300
g) and methylhydrogen cyclic siloxanes (34 g) were added and the mixture held at 70 °C for
an additional three hours. Hexamethyldisiloxane (24 g) was added with additional heating at
70 °C for an additional two hours. After cooling, NaHCO3 (2 g) was added and the mixture
washed three times with water (1500 g total). Volatiles were stripped at 50°C under reduced
15   pressure to produce a white solid product (310 g). The white solid product was identified by
^{29}Si NMR as a silsesquioxane resin having the average molecular formula:
$(Me_3SiO_{1/2})_{0.10}(MeHSiO_{2/2})_{0.19}(PhSiO_{3/2})_{0.71}$ where Me denotes methyl and Ph denotes
phenyl. This silsesquioxane resin was then used to prepare a Masterbatch according to the
procedure outlined above. The Masterbatch, produced with 8 weight percent of the candidate
20   resin and 0.3 weight percent of char catalyst, was then mixed with the thermoplastic resin at a
weight ratio of thermoplastic resin to Masterbatch of 10:1 in a twin-screw extruder, molded
according to the UL 94 test piece procedure and subjected to UL94 Flame Test. The final
formulation is shown in Table 1 below. The results are shown in Table 2 below.

Example 4

About 3 weight percent of Polytetrafluoroethylene Powder was added to the
Masterbatch prepared in Example 1 with polycarbonate as the plastic resin. This Masterbatch,
produced with 8 weight percent of the candidate resin and 0.3 weight percent of char catalyst,

5   was then mixed with thermoplastic resin at a weight ratio of thermoplastic resin to
Masterbatch of 10:1 in a twin-screw extruder, molded according to the UL 94 test piece
procedure and subjected to UL94 Flame Test. The final formulation is shown in Table 1
below. The results are shown in Table 2 below.

10   Example 5

About 3 weight percent of Polytetrafluoroethylene Powder was added to the
Masterbatch prepared in Example 2 with polycarbonate as the plastic resin. This Masterbatch,
produced with 8 weight percent of the candidate resin and 0.3 weight percent char catalyst,
was then mixed with thermoplastic resin at a weight ratio of thermoplastic resin to

15   Masterbatch of 10:1 in a twin-screw extruder, molded according to the UL 94 test piece
procedure and subjected to UL94 Flame Test. The final formulation is shown in Table 1
below. The results are shown in Table 2 below.

Example 6

20   About 3 weight percent of Polytetrafluoroethylene Powder was added to the
Masterbatch prepared in Example 3 with polycarbonate as the plastic resin. This Masterbatch,
produced with 8 weight percent of the candidate resin and 0.3 weight percent char catalyst,
was then mixed with thermoplastic resin at a weight ratio of thermoplastic resin to
Masterbatch of 10:1 in a twin-screw extruder, molded according to the UL 94 test piece

25   procedure and subjected to UL94 Flame Test. The final formulation is shown in Table 1
below. The results are shown in Table 2 below.

<center>Comparison Example 1</center>

Masterbatch containing $(Me_2HSiO_{1/2})_{0.22}(PhSiO_{3/2})_{0.54}(PrSiO_{3/2})_{0.23}$ where Me denotes methyl, Ph denotes phenyl, and Pr denotes propyl.

5   A phenyl propyl silicone resin in solid flake form (1000 g) was dissolved in toluene (667 g), heated to remove residual water via azeotropic distillation, and cooled to ambient temperature. Dimethylchlorosilane (490 g) was added to the solution and the mixture heated to 39°C for three hours, then stirred at ambient temperature for 18 hours. Volatile material was removed until the head temperature reached 110 °C, then the mixture cooled to 30 °C.

10   Water (45.8 g) was added and removed via azeotropic distillation, additional water (100 g) added and azeotropically removed, then isopropanol (88 g) added and all volatiles removed by distillation at ambient, then reduced, pressure. The hot molten material was poured onto a cooled metal surface. A portion of the resulting friable solid (502.2 g) was dissolved in dimethoxyethane (500.1 g) and mixed with dimethylchlorosilane (72.3 g). The mixture was

15   heated to 35 °C for four hours, then concentrated under reduced pressure to a viscous liquid. Additional dimethoxyethane (310.1 g) and deionized water (50.0 g) were added and all volatiles removed under reduced pressure. Again, dimethoxyethane (199.9 g) and deionized water (39.7 g) were added and heated to reflux for 90 minutes, then all volatiles removed under reduced pressure. The hot molten product was poured onto a cooled metal surface.

20   The resulting product was isolated as a friable solid. The product was identified by ^{29}Si NMR as a silsesquioxane resin having the average molecular formula: $(Me_2HSiO_{1/2})_{0.22}(PhSiO_{3/2})_{0.54}(PrSiO_{3/2})_{0.23}$ where Me denotes methyl, Ph denotes phenyl, and Pr denotes propyl. This silsesquioxane resin was then used to prepare a Masterbatch according to the procedure outlined above. The Masterbatch, produced with 8

25   weight percent of the candidate resin and 0.3 weight percent of char catalyst, was then mixed with the thermoplastic resin at a weight ratio of thermoplastic resin to Masterbatch of 10:1 in a twin-screw extruder, molded according to the UL 94 test piece procedure and subjected to UL94 Flame Test. The final formulation is shown in Table 1 below. The results are shown in Table 2 below.

30

Comparison Example 2

A Masterbatch, with polycarbonate as the plastic resin, was prepared using the procedure outlined above using Toshiba XC99-B5664 (a siloxane resin having the average

5   molecular formula $(Me_3SiO_{1/2})_{0.121}(Me_2SiO_{2/2})_{0.157}(PhSiO_{3/2})_{0.578}(MeSiO_{3/2})_{0.145}$ where Me denotes methyl and Ph denotes phenyl) as the Siloxane Resin. This Masterbatch, produced with 8 weight percent of the candidate resin and 0.3 weight percent of char catalyst, was then mixed with thermoplastic resin at a weight ratio of thermoplastic resin to Masterbatch of 10:1 in a twin-screw extruder, molded according to the UL 94 test piece

10   procedure and subjected to UL94 Flame Test. The final formulation is shown in Table 1 below. The results are shown in Table 2 below.

Comparison Example 3

Masterbatch containing $(Me_3SiO_{1/2})_{0.188}(PhSiO_{3/2})_{0.812}$ where Me denotes methyl and

15   Ph denotes phenyl.

A mixture of phenyltrichlorosilane (720.1 g) and trimethylchlorosilane (92.8 g) were hydrolyzed with a mixture of water (640 g) and toluene (519.9 g) cooled in an ice bath. The reaction mixture was heated to 80 °C for 3 hours, then 90°C for 18 hours. Aqueous sodium chloride, additional toluene and a small amount of methanol were added to facilitate the

20   phase removal of the aqueous phase. The portion of mixture that was not readily phase separating was filtered and the organic layers combined and heated to 66 °C for 40 minutes. This was washed sequentially with saturated aqueous $NaHCO_3$ and aqueous NaCl. Residual water was removed via azeotropic distillation. The product mixture was again filtered, then solvent removed by stripping under reduced pressure and the hot molten product was poured

25   onto a cooled metal surface. The resulting product was isolated as a friable solid. The product was identified by ^{29}Si NMR as a silsesquioxane resin having the average molecular formula: $(Me_3SiO_{1/2})_{0.188}(PhSiO_{3/2})_{0.812}$ where Me denotes methyl and Ph denotes phenyl. This silsesquioxane resin was then used to prepare a Masterbatch according to the procedure outlined above with polycarbonate as the plastic resin. The Masterbatch, produced

30   with 8 weight percent of the candidate resin and 0.3 weight percent of char catalyst, was then mixed with the thermoplastic resin at a weight ratio of thermoplastic resin to Masterbatch of

10:1 in a twin-screw extruder, molded according to the UL 94 test piece procedure and subjected to UL94 Flame Test. The final formulation is shown in Table 1 below. The results are shown in Table 2 below.

5   Comparison Example 4

About 3 weight percent of Polytetrafluoroethylene Powder was added to the Masterbatch prepared in Comparison Example 3. This Masterbatch, produced with 8 weight percent of the candidate resin and 0.3 weight percent char catalyst, was then mixed with thermoplastic resin at a weight ratio of thermoplastic resin to Masterbatch of 10:1 in a twin-

10   screw extruder, molded according to the UL 94 test piece procedure and subjected to UL94 Flame Test. The final formulation is shown in Table 1 below. The results are shown in Table 2 below.

Table 1

Final Formulation

Example	Thermoplastic Resin (balance to 100 wt%)	Wt% Silsesquioxane Resin	Wt% Char Catalyst	Wt% Teflon 6C
1	CALIBRE® 200-22	0.8	0.03	0.0
2	"	0.8	0.03	0.0
3	"	0.8	0.03	0.0
4	"	0.8 [a]	0.03	0.3
5	"	0.8 [b]	0.03	0.3
6	"	0.8 [c]	0.03	0.3
CE1	"	0.8	0.03	0.0
CE2	"	0.8	0.03	0.0
CE3	"	0.8	0.03	0.0
CE4	"	0.8[d]	0.03	0.3

[a] same silsesquioxane resin as used in example 1

5　　[b] same silsesquioxane resin as used in example 2

[c] same silsesquioxane resin as used in example 3

[d] same silsesquioxane resin as used in comparative example 3

Table 2

FR Additive*	Flame Time (seconds)			Cotton Ignition	UL 94 Rating
	Set 1	Set 2	Total 1+2		
Example 1	22	17	39	Y	2
Example 2	11	18	29	N	0
Example 3	15	14	29	Y	2
Example 4	36	41	77	N	0
Example 5	7	17	24	Y	2
Example 6	9	20	29	N	0
Comparison Example 1	105	16	121	Y	2
Comparison Example 2	57	41	98	Y	2
Comparison Example 3	51	37	88	Y	2
Comparison Example 4	44	56	100	Y	2
Emerge® 8500*	30	47	77	Y	2

* test sample dimension 125 x 13 x 1 mm

Examples 7-26 and Comparison Examples 5-9

A Masterbatch containing 10 or 50 weight percent of a silsesquioxane resin having
the average molecular formula $(MeHSiO_{2/2})_{0.25}(PhSiO_{3/2})_{0.75}$ where Me denotes methyl
and Ph denotes phenyl were produced according to the procedure outlined above. The
5   specific thermoplastic resin used in the fire test is described in Table 2 below and was mixed
with the Masterbatch in a 10:1 weight ratio mixture of thermoplastic resin to Masterbatch in a
twin-screw extruder. The final formulation is shown in Table 3 below. All of these Fire
Retarded experiments were performed using ASTM E 1354 with an external heat flux at 90
kW/m^2. In Table 3, a negative number denotes a reduction of Fire Retardant feature (an
10   improvement) when compared to the virgin resin or blend. For example, the Heat Release
Rate is reduced (negative) and is a slower burning fire, thus improved. In Comparison
Examples 5-9, non-char forming materials, the Heat Release Rate is positive, thus not an
improvement. By virgin, it is meant that the candidate plastic resin is not altered in any way
before the burn. It is simply injection molded into the plaques described. The virgin blend is
15   simply the mixture of polycarbonate blended with ABS, PBT, etc. at 85 wt% polycarbonate
and 15 wt% blended polymer, also unaltered and molded.

Table 3

Example	Thermoplastic or Thermoset Resin Type (balance to 100 wt%)	Wt% silsesquioxane resin	Wt% Char Catalyst	Wt% Teflon 6C	Delta Avg HRR-Control	Delta Peak Heat Release	Delta Peak CO Release kg/kg	Delta Peak CO2 Releas
7	PELLETHANE® 2355-75A	1	0.03	0.3	-110	-944	-0.0084	-3.8
8		1	0.00	0.0	-24	-768.5	-0.07255	-6.2
9		5	0.03	0.3	-692	-1443	0.28825	-0.8
10		5	0.00	0.0	-286.5	-690.5	-0.6248	-17.3
11		Virgin			0	0	0	
12	CALIBRE® 200-22 (85%)	1	0.03	0.3	-478.5	-738	0.3825	7.0
13	CRASTIN® 6129 (15%)	1	0.00	0.0	-243.5	-630.5	8.9275	180.
14		5	0.03	0.3	-535	-1013.5	0.3635	7.
15		5	0.00	0.0	-437	-720	2.54675	61.
16		Virgin blend			0	0	0	
17	CALIBRE® 200-22 (85%) MAGNUM® (15%)	1	0.03	0.3	-1002.5	-521	0.195	;
18		1	0.00	0.0	-1405.5	-1638	1.0455	20.
19		5	0.03	0.3	-1036	-657	2.4795	28.
20		5	0.00	0.0	-189	-46	0.20545	4.
21		Virgin blend			0	0	0	
22	CRASTIN® 6129	1	0.03	0.3	-131	-585.5	-1.1642	-43.1
23		1	0.00	0.0	-2694	4200	-1.6595	-5<
24		5	0.03	0.3	-1033	-1500	1.5329	-52.
25		5	0.00	0.0	662	141.5	-1.375	-46.
26		Virgin			0	0	0	
Comparison Example 5	AMOCO® 4018	1	0.03	0.3	514	57.5	-0.35315	-1.5
Comparison Example 6		1	0.00	0.0	233	768.5	8.11185	174.4
Comparison Example 7		5	0.03	0.3	1893	2125.5	-0.34365	1.7
Comparison Example 8		5	0.00	0.0	248.5	332.5	2.08335	35.5
Comparison Example 9		Virgin			0	0	0	

The examples of the invention provide thermoplastics with excellent flame retardant

5   behavior without the use of Polytetrafluoroethylene Powder (Teflon®) halogen-containing

additives. Addition of Polytetrafluoroethylene Powder to the flame retarded compositions of

this invention in some cases further improved the flame retardant and UL94 behavior of the

compositions of this invention.